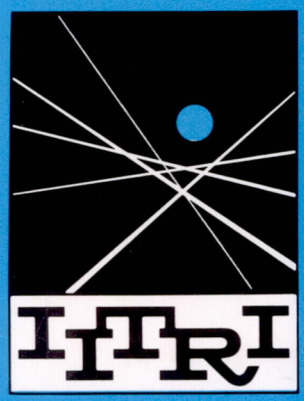

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Technology Center Chicago 16, Illinois

Report No. IITRI-C6018-3
(Quarterly Report)

INVESTIGATION OF LIGHT SCATTERING IN HIGHLY REFLECTING PIGMENTED COATINGS

UNPUBLISHED PRELIMINARY DATA

National Aeronautics
and Space Administration
Office of Advanced Research
and Technology

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INVESTIGATION OF LIGHT SCATTERING IN HIGHLY REFLECTING PIGMENTED COATINGS

July 1, 1963, to October 1, 1963

Contract No. NASr-65(07)
IITRI Project C6018

Prepared by

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of

IIT RESEARCH INSTITUTE
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Chicago 16, Illinois

for

National Aeronautics and Space Administration
Office of Advanced Research and Technology
Washington, D. C.

Copy No. 22

October 11, 1963

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FOREWORD

This is Report No. IITRI-C6018-3 (Quarterly Report) of Project C6018, Contract No. NASr-65(07), entitled, "Investigation of Light Scattering in Highly Reflecting Pigmented Coatings." This report covers the period from July 1, 1963 to October 1, 1963.

Major contributors to the program include Gene A. Zerlaut (Project Leader), Dr. S. Katz (theoretical analyses), J. Stockham and V. Razinuas (laboratory studies), and Douglas G. Vance (reflectance and transmittance measurements). G. Langer, P. Schossberger, and J. Allen also contributed to the program during the first quarter. Contributions to this report were made by Dr. S. Katz and J. Stockham.

Data are recorded in logbooks C14085 and C13906.

Respectfully submitted,

IIT RESEARCH INSTITUTE

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Approved by:

Theodore H. Meltzer
Manager
Polymer Research

GAZ/dbn

ABSTRACT

INVESTIGATION OF LIGHT SCATTERING
IN HIGHLY REFLECTING PIGMENTED COATINGS 10089

Investigations were conducted to prepare carefully designed arrays of silver halide crystals as models for elucidation of the light scattering behavior of closely packed systems. The problems associated with the preparation of the silver halide arrays are described. Also discussed are the techniques used to measure the particle size and the optical properties of the crystals. An analysis of the pertinent optical properties is expected to provide an understanding of light-scattering behavior of particles. Such an understanding should provide insight into the behavior of highly reflecting pigmented systems. An analysis of the application light-scattering concepts is in progress and is therefore outlined in order to provide a basis for future studies.

AUTHOR

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INVESTIGATION OF LIGHT SCATTERING IN HIGHLY REFLECTING PIGMENTED COATINGS

I. INTRODUCTION

This portion of the study is an examination of light scattering theory. Its purpose is to define the parameters controlling the scatter of light by small particles and thus to assist in the selection of optimum pigment materials for control of the reflective and emissive properties of surfaces.

A. Concept of Light Scattering by Particles

When light or a related electromagnetic radiation impinges on a particle, the interaction leads to a redistribution of the radiant energy. The resulting radiation, which may be regarded as originating at the particle, is termed the light scattered by the particle. The particle is differentiated from the medium in which it resides by its refractive index. This refractive index may be real or complex--a concept which requires further consideration.

The solutions of the electromagnetic wave equation for transparent and absorbing material leads to a generalized expression for the refractive index which includes terms for both refraction and absorption. The so-called "complex refractive index," n^*, can be defined by the relation

$$n^* = n\,(1 - i\,K) \qquad (1)$$

For a substance whose absorption coefficient is μ, it is shown[1] that K in Equation 1 is defined by

$$\mu = \frac{4\pi K}{\lambda} \qquad (1a)$$

where λ is the wavelength of the light.

The n in Equation 1 is not analogous to the refractive index defined by Snell's law; Snell's law is not obeyed for transmitting media with absorption.[2] In the limit, as the absorption diminishes to zero and the medium becomes transparent, n^* becomes equal to n and Snell's law applies.

In addition to systems with real and complex refractive indices, a third case exists, that of a perfectly reflecting surface. Expressed in terms of electromagnetic theory, this condition may be described as the upper limiting value of n, i.e., $n \longrightarrow \infty$.[3]

In the present plan of the study, we shall attempt to apply light-scattering theory to each of the three classes of particles. When possible, it is planned to examine (1) the total scatter of single particles and (2) the angular distribution of scattered intensity.

---

[1]Sinclair, D. and La Mer, V. K. Chem. Rev. 44, 245 (1949).

[2]Ditchburn, R. W., "Light," Interscience Publishers, Inc., pp. 441, 480, 1953.

[3]Van de Hulst, H. C., "Light Scattering by Small Particles," Wiley p. 119, 1957.

Multiple scattering and the scatter of more complicated forms will be attempted later. Primary attention will be directed toward spherical particles, which have been discussed most extensively. In the literature, less attention has been devoted to cylindrical, cubic, and spiral particles.

Throughout the discussion, incoherent, unpolarized incident light is considered, and the scattering is limited to light with the same wavelength as the incident light.

B. Light Scattering by Transparent Isotropic Particles

Historically, the scattering of light by small particles was first discussed quantitatively by Rayleigh.[4] He considered the case of spherical particles which were much smaller than the wavelength of the scattered light. For these transparent spherical particles, the amount of light of wavelength λ scattered by a sphere of radius r per unit intensity of illumination (unit energy/unit area of cross section) is given by

$$S = 24\pi^3 \left(\frac{n^2 - 1}{n^2 + 2}\right)^2 \frac{V^2}{\lambda^4} \qquad (2)$$

where V = the volume of the particle

n = the refractive index of the particle

S = the effective scattering area or the scattering cross section of one sphere.

---

[4] Lord Rayleigh, "Scientific Papers," Cambridge University Press, Vol. 1, 1899, and Vol. 4, 1903.

Equation 2 applies to very small particles of molecular dimensions without regard to shape. It is applicable to spherical particles where $r < 0.1\ \lambda$. The familiar relationships for Rayleigh scattering, which state that the scattered energy of small particles varies directly as the sixth power of the particle radius and inversely as the fourth power of the wavelength, are evident in Equation 2.

Mie[5] examined the general problem where no restriction is applied to the particle size. His analysis employed classical electromagnetic theory to examine the diffraction of a plane wave by a sphere of any composition. In Mie's treatment, the possibility of conductivity or absorption in both the external medium and the sphere is considered by assigning to each a complex index of refraction. We shall follow the usual practice and consider only a real refractive index in the external medium. The discussion here is limited to spheres of real finite refractive index. Other cases will be examined later.

When a beam of light passes through a monodisperse suspension of spherical particles of radius r, the transmission, T, is given by

$$T = e^{-K \pi r^2 n \ell} \qquad (3)$$

---

[5]Mie, G., Ann. Physik 25, 377 (1908); Stratton, J. A., "Electromagnetic Theory," McGraw Hill, Chapter IX, 1941.

where n = the particle concentration per unit volume

ℓ = the path length.

K is the energy scattered per unit area of particle cross section per second. K is equal to the scattering area, S, divided by πr^2. It is described by various authors as the effective scattering cross section, the total Mie coefficient, and the extinction cross section. It should be noted that extinction cross section is a somewhat more general term than scattering cross section, and only in the case of nonabsorbing particles is it equivalent to the scattering cross section.

Mie's analysis defined K as the sum of a convergent series.

$$K(\alpha, n) = \frac{2}{\alpha^2} \sum_{m=1}^{\infty} (2m + 1) \left[|a_m|^2 + |b_m|^2 \right] \quad (4)$$

where n = refractive index of the particle in the medium

$\alpha = \frac{2\pi r}{\lambda}$, a size parameter

$\beta = n\alpha$

r = particle radius

λ = wavelength of the light

The vertical lines in Equation 4 indicate that the absolute value of the complex argument is to be used. a_m and b_m are complex numbers termed amplitude functions. They are

$$a_m = (-1)^{m + 1/2} \frac{S'(\beta) S(\alpha) - n S'(\alpha) S(\beta)}{S'(\beta) \phi(\alpha) - n \phi'(\alpha) S(\beta)} \quad (4a)$$

$$b_m = (-1)^{m + 3/2} \frac{n S'(\beta) S(\alpha) - S'(\alpha) S(\beta)}{n S'(\beta) \phi(\alpha) - \phi'(\alpha) S(\beta)} \qquad (4b)$$

where $$S(Z) = \frac{\pi Z}{2}^{1/2} J_{m + 1/2}(Z)$$

$$\phi(Z) = S(Z) + i C(Z)$$

$$C(Z) = (-1)^m \frac{\pi Z}{2}^{1/2} J_{-m - 1/2}(Z)$$

The J's represent Bessel functions of the indicated order, and the primed terms are their derivatives with respect to Z.

It can be shown that Equation 4 reduces to Equation 2 for very small values of r, i.e., that Rayleigh scattering is a limiting case of Mie scattering.

Representative plots of the total Mie coefficient, K, with respect to the parameter α for two refractive indices are reproduced in Figure 1. The first maximum is higher and is displaced toward the origin with increasing n.

A number of tabulations of K are available. Both Van de Hulst[3] and Penndorf[6] list compilations of data and also have extensive bibliographies of source material.

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[6]Penndorf, R., New Tables of Scattering Functions, Geophysics Research Papers, No. 40, AFCRC-TR-56-204(6), Part 1-6.

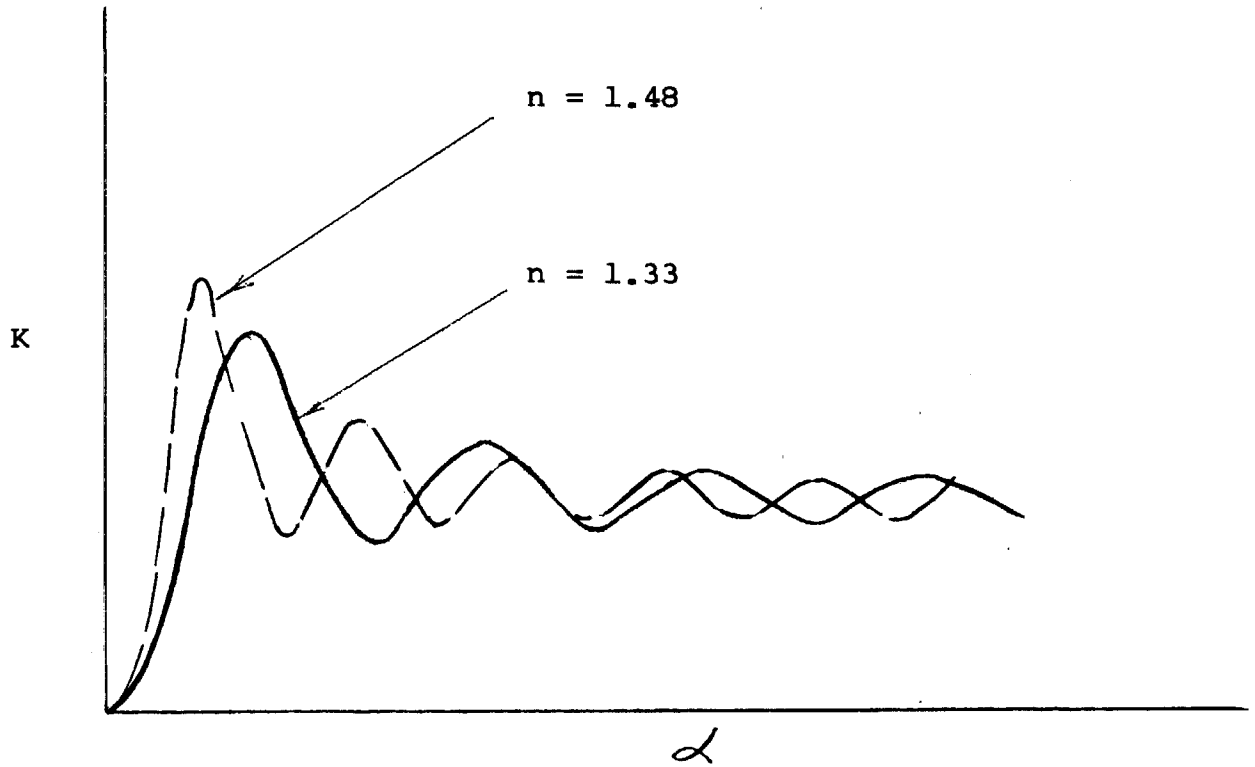

Figure 1

TOTAL MIE SCATTERING COEFFICIENT
FOR REFRACTIVE INDICES OF 1.33 and 1.48

For many applications, the angular or radial distribution of the scattered energy is required. For unpolarized incident radiation of intensity I_o, the radiation scattered in the direction θ (the angle between the incident and the scattered beam) is

$$I(\theta, n) = \frac{I_o}{a^2} (i_1 + i_2) \tag{5}$$

The quantities i_1 and i_2 are called intensity functions. They are proportional to the two mutually perpendicular plane polarized components of the light scattered by the particle in the direction θ. The intensity functions are

$$i_1 = \left| \sum_{m=1}^{\infty} \frac{2m+1}{m(m+1)} \left(a_m \pi_m + b_m \tau_m \right) \right|^2 \tag{5a}$$

and

$$i_2 = \left| \sum_{m=1}^{\infty} \frac{2m+1}{m(m+1)} \left(a_m \tau_m + b_m \pi_m \right) \right|^2 \tag{5b}$$

Again, the vertical lines indicate that the absolute values of the complex arguments are to be used. a_m and b_m have the same values as before. π_m and τ_m are derivative functions of the corresponding Legendre polynomial, P_m, of order m, thus

$$\pi_m = \frac{d P_m}{dx} \tag{5c}$$

and

$$\tau_m = \pi_m x - (1 - x^2) \pi'_m \tag{5d}$$

where $x = \cos \theta$.

Tables of amplitude functions have been prepared by Penndorf,[6] Gumprecht and Sliepcevich,[7] and others. Many authors, including Lowan,[8] have tabulated the angular scattering functions for various values of the parameter α and various refractive indices. In the case of transparent scatterers, certain characteristics are noted. Maxima always occur in the forward and backscattered directions, and the intensities of these maxima are the same for both of the polarized components of scattering. Also, as the size of the particle increases with respect to the wavelength of the scattered light, the scattering in the forward direction increases very rapidly. Some representative angular scattering patterns are shown in Figure 2.

---

[7] Gumprecht, R. O., and Sliepcevich, C. M., "Tables of Light Scattering Functions for Spherical Particles," University of Michigan, 1951.

[8] Lowan, A. N., "Tables of Scattering Functions for Spherical Particles," National Bureau of Standards, 1949.

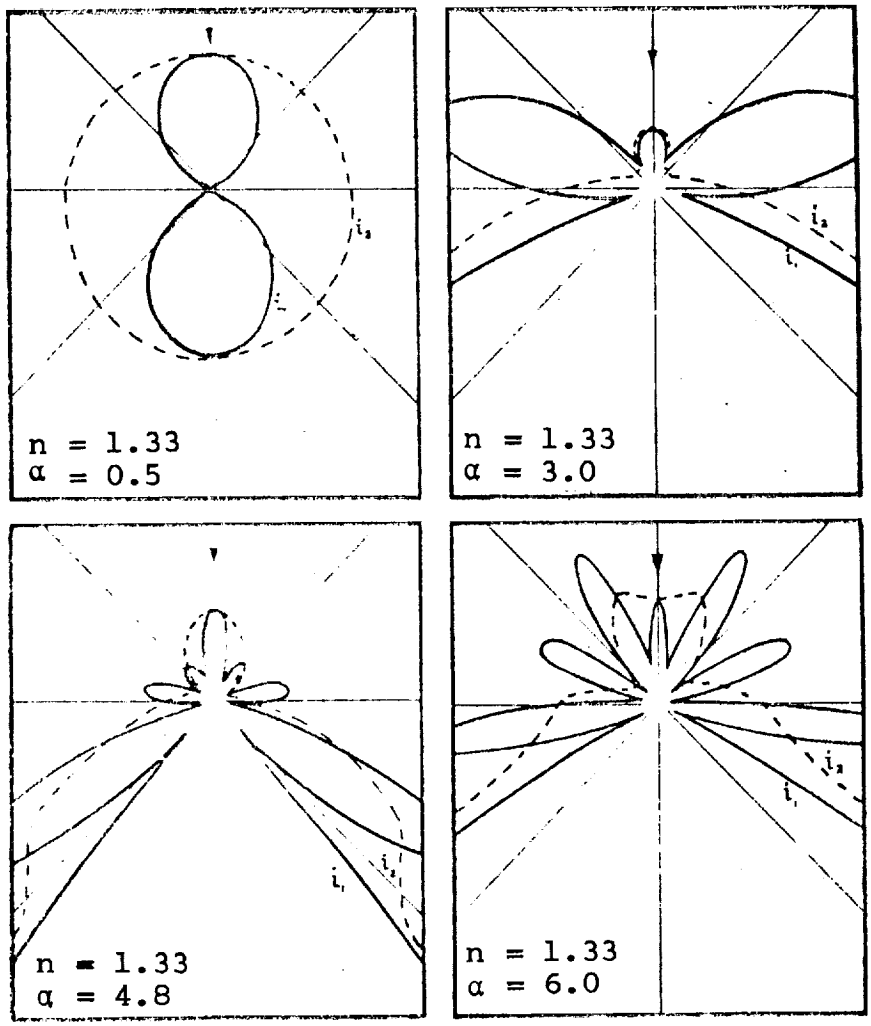

Figure 2

RADIAL DISTRIBUTION OF INTENSITY
OF LIGHT SCATTERED BY SPHERICAL PARTICLES

II. EXPERIMENTAL WORK

A. Preparation of Sols

Suspensions of silver halide crystals are being used to study the dependence of light scattering on the size and concentration of particles. The basic procedures adapted for the preparation of the suspension are those described by Berry.[9,10] The silver halide crystals are precipitated by the simultaneous addition at equal rates of 1.96 N solutions of silver nitrate and of potassium halide into a 3% solution of gelatin at 50°C. The apparatus for the preparation is shown in Figure 3. Warm water from a constant-temperature bath is circulated between the walls of a double-wall vessel containing 100 ml of gelatin solution; the circulating water temperature is sufficient to maintain the gelatin solution at 50°C. The gelatin solution is stirred during the chemical addition by a magnetic stirrer. The reactants are added from 50-ml syringes at the rate of 2 ml/min until a total of 30 ml of each reagent has been introduced into the gelatin solution; feed rates are controlled by a Harvard infusion-withdrawal pump adapted to operate the two syringes simultaneously. Chemical addition rates are sufficient to quickly reach and maintain a high degree of supersaturation; thus, crystal growth is not dependent upon the presence of imperfections. The gelatin prevents coalescence of the crystals.

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[9] Berry, C. R., J. Opt. Soc. Am. 52, 888 (1962).

[10] Berry, C. R., Phot. Sci. and Eng. 5, 332, (1961).

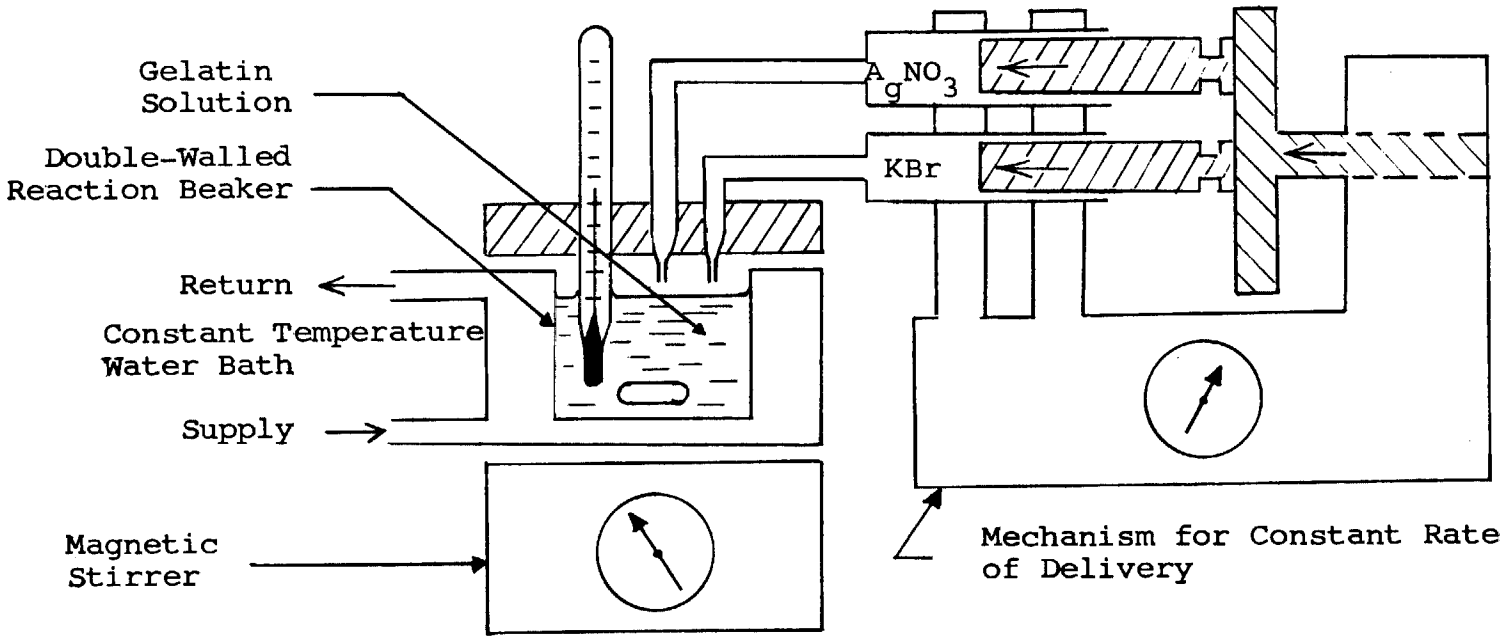

Figure 3

CRYSTAL GROWTH APPARATUS

Both silver bromide and silver chloride crystals have been prepared by the described procedures. Silver chloride has some advantage since it is white and not a pale yellow as is the bromide. The particle size of the crystals is controlled by the temperature, the amount of chemicals added, and the solvent addition. The lower the reaction temperature, the more viscous the gelatin and the smaller the crystal sizes. Large chemical additions provide larger nuclei and thus larger particles. The addition of a solvent such as ammonia also yields larger particles.

The halides are quite sensitive to light; thus, the preparations are carried out under a red safety light in a darkroom. A photographic grade of inert gelatin, provided through the courtesy of the Atlantic Gelatin Co., is used. An excess of potassium bromide, added after the simultaneous additions, is a good desensitizer; an excess of potassium chloride is not nearly as effective an inhibitor. However, a small excess of potassium bromide added with a greater excess of potassium chloride is a good inhibitor; it does not produce a yellowing of the silver chloride crystals as is the case when a large excess of potassium bromide is added to the silver chloride suspensions. In spite of the precautions taken to desensitize the crystals, they still degrade due to the intensity of light beam in the instruments used to measure light scattering; further improvement is required in this area.

B. Measurement of Crystal Size

The crystal sizes are determined from electron microscope analysis of samples prepared in the following manner. In the darkroom, an aliquot of the freshly prepared silver chloride suspension is diluted 1:100 in distilled water. A stainless steel electron microscopic screen bearing a Formvar film is dipped into this suspension, withdrawn, the excess fluid wicked off, and the screen allowed to dry. After drying, the screen is placed in a vacuum evaporator, and after shadow-casting with platinum at an angle of 18°, the screen is directly cast with carbon. The cast screens are then placed in an acid fix (Kodak F-5) for 3 hr to remove the silver halide crystals; well-defined replicas of the crystal shape and size are obtained. After washing and drying, the screens are examined in an electron microscope and representative areas are photographed. Figure 4 is typical of the crystals prepared. These crystals measure about 0.2 μ or each edge.

C. Preparation of Films

Transmission and reflectance measurements of various crystal arrays as a function of wavelength can be studied with a Cary model 14 recording spectrophotometer and the Perkin Elmer 137 sodium chloride spectrophotometer. The Cary instrument covers the wavelength range 0.2 to 2.6 μ for transmission studies and 0.3 to 2 μ for reflectance studies. The Perkin Elmer instrument is used for transmission studies in the infrared range of 2.5 to 15 μ.

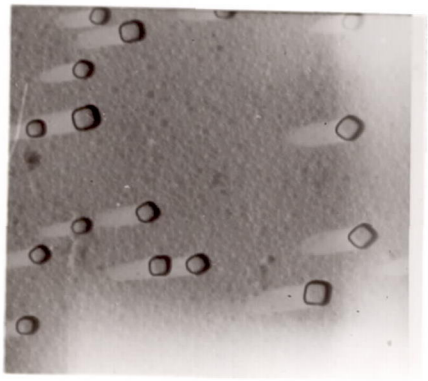

Figure 4

SILVER CHLORIDE CRYSTALS
(15,000X)

For reflectance measurements, flat surfaces for mounting the crystal suspensions were prepared from 2-in. diameter aluminum stock. These discs are overlaid with a thin Collodion film before the application of the crystal suspension. Application of the crystals directed on the aluminum results in a chemical exchange reaction; the suspension turns black, evidently from the formation of free silver.

For transmission studies, a Collodion film is stretched over an aperture cut in a plastic or aluminum mount to fit the sample holder in the instruments. The Collodion film is deposited on a glass microscope slide and stripped from the slide to a water surface, where it is scooped up with the mount. A hot plate set at a moderate temperature quickly dries the film and stretches it taut across the aperture.

The suspensions of silver halide crystals are deposited directly on the Collodion surface with the aid of the Gardner knife. The blank, cut from the mounts to fit the aperture opening, supports the Collodion film during the application of the suspension. The viscosity of the suspension must be controlled during the application and depends on the concentration of gelatin and the temperature at which the suspension is applied to the Collodion film. At high viscosity the suspensions flow under the knife and destroy thickness control. High-viscosity suspensions result in the formation of uneven films due to agglomeration of the gelatin. It was found best to apply the crystals at a temperature of 20 to 40°C. A 2:1 dilution of the gelatin

suspension gave a dry film approximately one-half the thickness of that obtained with the original suspension.

Application of a suspension results in some distortion of the Collodion film. Thus, the dried suspensions may vary from 10 to 17 x 10^{-4} in. in thickness with the knife blade setting at 10^{-4} in. Spreading of the suspension on the Collodion film before removing it from the glass slide was attempted, but these coated films were difficult to strip from the slide.

The thickness of the films can be measured to a precision of $\pm$ 5 x 10^{-5} in. with a spring-loaded Ames micrometer. A magnetic micrometer is also available if ferrous mounts should prove desirable.

D. Transmission and Reflectance Measurements

The transmission and reflectance measurements were made with a Cary model 14 recording spectrophotometer equipped with a model 1411 reflectance attachment. Two types of illumination are possible, dispersed, nondiffuse (type 1) and nondispersed, diffuse (type 2). Type 1 illumination can be provided with an integrating sphere or with a ring collector. With the integrating sphere, chopped monochromatic radiation from the signal generator of the spectrophotometer is alternately directed at 30 cps to the reference and sample ports in the sphere. Radiation alternating from the sample and reference materials is diffusely reflected within the sphere and is viewed by the phototube; with the ring collector, the sample is illuminated at normal incidence with

chopped monochromatic light. The phototube alternately receives radiation from a mirror collector viewing the sample at 45° and light from the reference beam.

In type 2 illumination, two lenses and a 45° mirror direct the nondispersed radiation from a 500-watt tungsten lamp through the bottom of the sphere to the sphere wall. The radiation is diffusely reflected within the sphere; this results in diffuse illumination of the sample and reference material. Radiation reflected from the sample and reference material passes through the appropriate sphere ports to the signal generator, where it is focused, chopped, and the sample and reference beams are alternately directed into the monochromator.

Figures 5 and 6 present reflectance curves for dried silver bromide and silver chloride films obtained by coating the aluminum disc with the silver halide suspension. Figure 7 is a transmission curve for the silver chloride suspension supported by Collodion. These curves were obtained with type 2 illumination. This type of illumination illuminates the sample with all wavelengths of light. Thus, the halides are undergoing decomposition during the measurements. Type 1 illumination might be better in this respect since the sample is illuminated by a dispersed beam (i.e., monochromatic light). Thus, materials sensitive to ultraviolet degradation would not be affected until the measurements are completed.

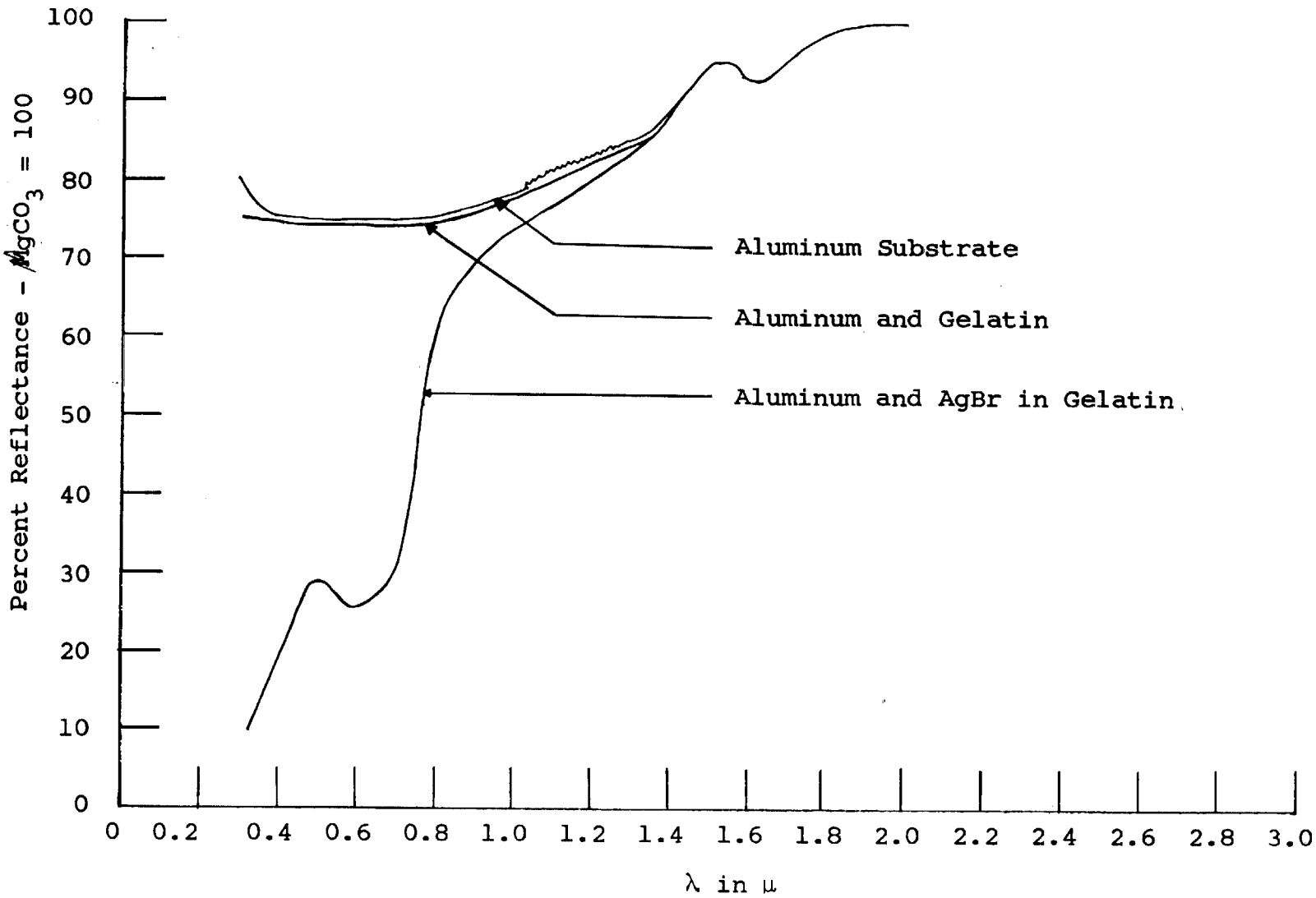

Figure 5

REFLECTANCE OF DRIED SILVER BROMIDE FILMS

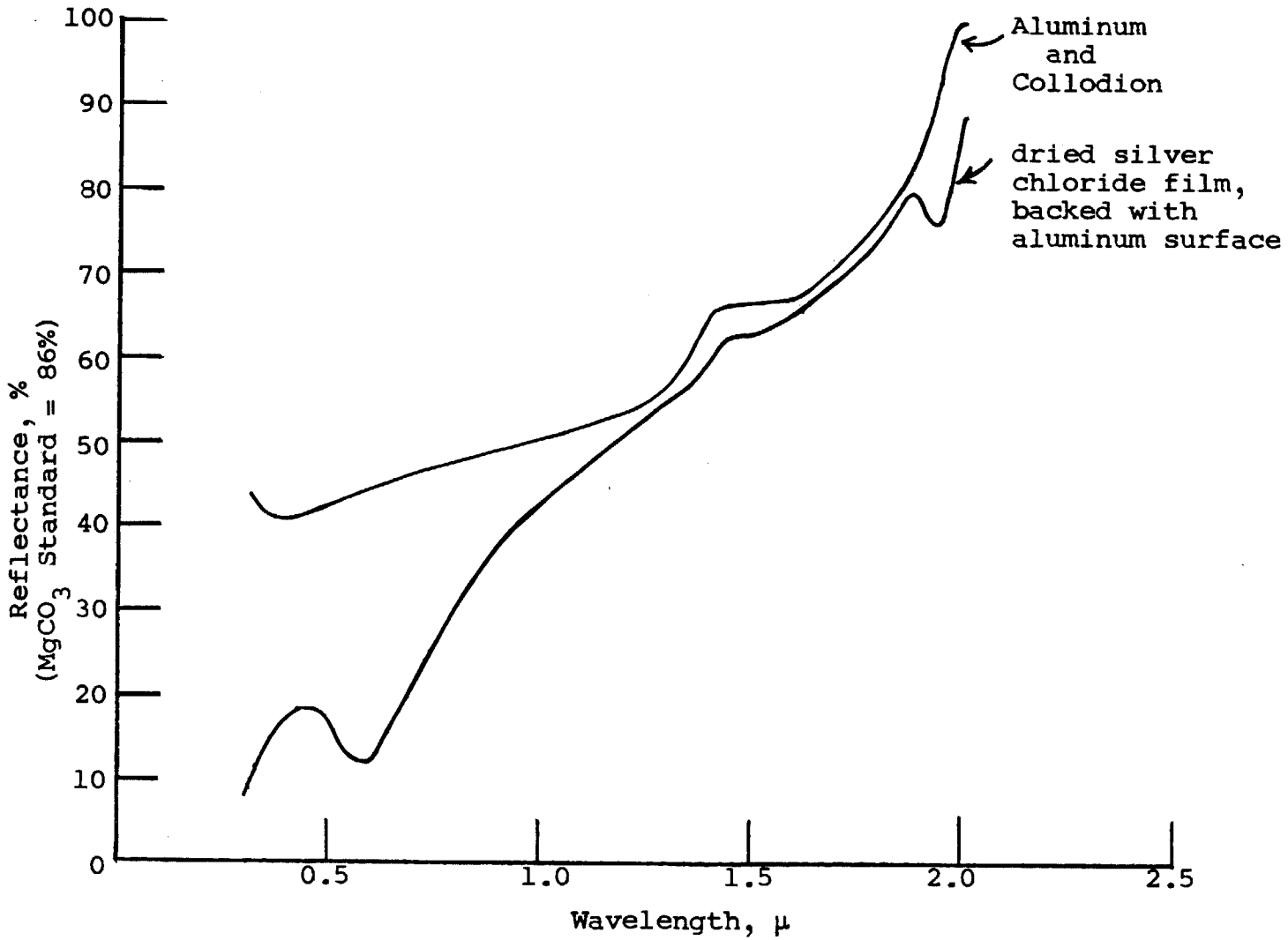

Figure 6

REFLECTANCE OF DRIED SILVER CHLORIDE FILMS

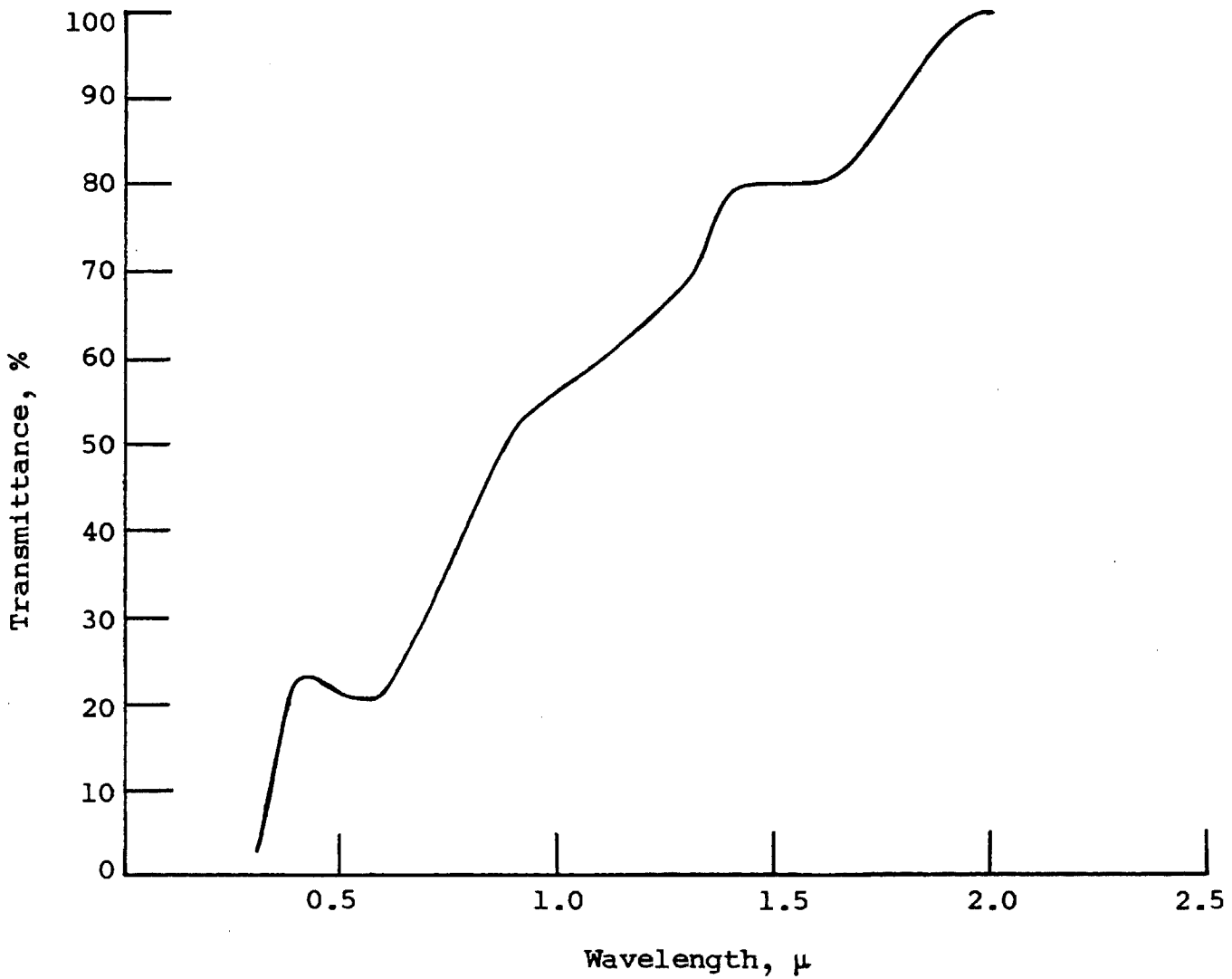

Figure 7

TRANSMITTANCE OF THIN SILVER CHLORIDE FILM

The similarity of the transmission and reflectance curves lead us to believe that the reflectance films were not thick enough, and the result is actually a transmission curve where the light passing through the film is reflected back through the film by the aluminum disc. A better method would be to replace the disc with a light trap so that the transmitted light is lost effectively and only the reflected light is measured.

The transmission pattern obtained for Saran wrap (Figure 8) is characteristic of interference patterns and suggests that the effect of the thickness of our halide film supports needs to be investigated. This type of pattern may be aggravated by the use of the diffused, nondispersed, incident light.

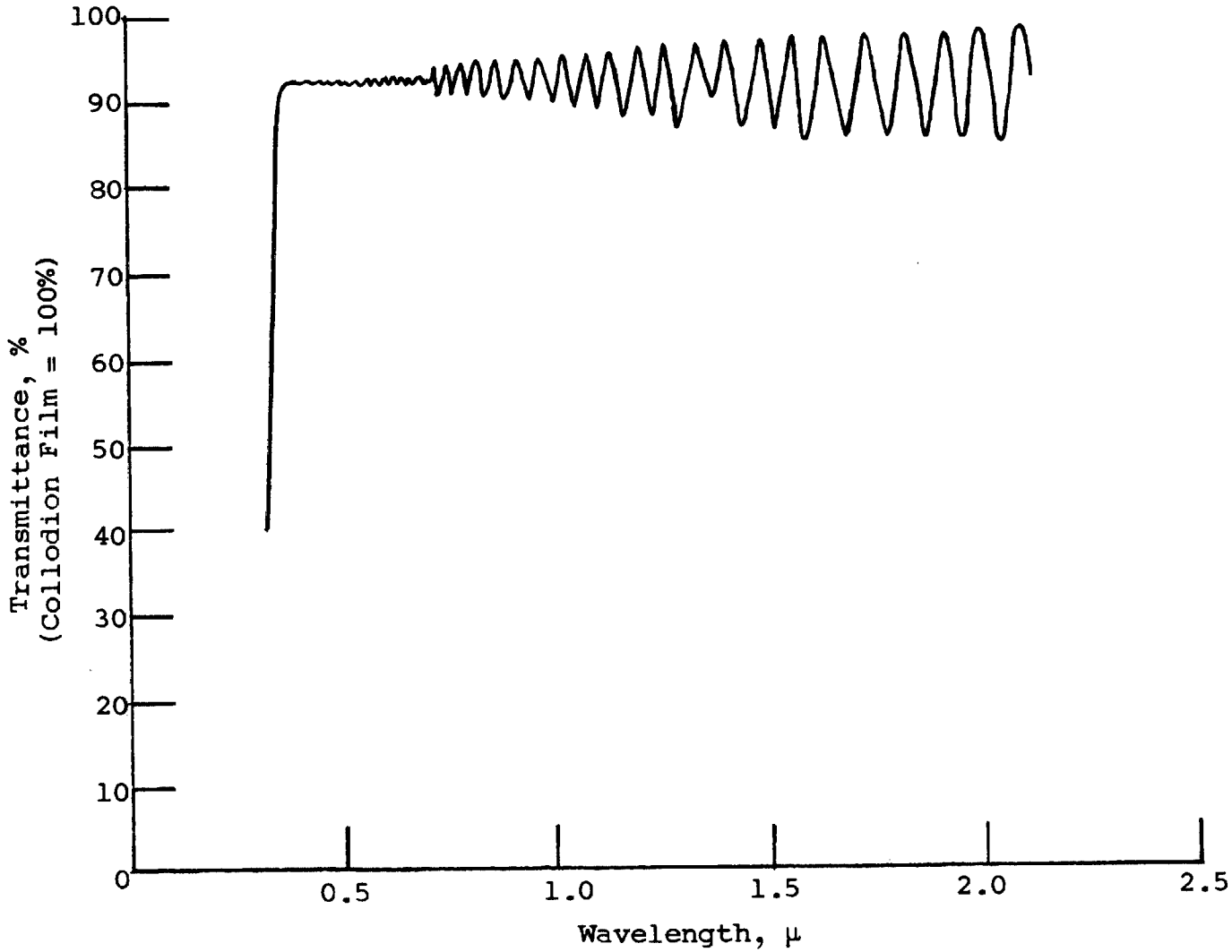

Figure 8

TRANSMITTANCE OF SARAN WRAP

III. FUTURE WORK

Although the procedures for preparing and analyzing the monodisperse silver bromide crystals are fairly well established, we have experienced some difficulty in the preparation of light-stable silver halide arrays. The use of a more suitable gelatin coupled with improved reflectance and transmittance measuring techniques using monochromatic rather than polychromatic illumination is expected to eliminate the principal problems encountered. Once the techniques have been refined, the dependence of light scattering on different arrays and concentrations of particles at various wavelengths of incident light can be determined.

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